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By P.L. Sibrell, S.R.M. Burton, and D.E. Cornelius
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Abbreviations and Acronyms Used in this Report

Ar	argon
Cr	chromium
DEG	diethylene glycol
GFAAS	graphite furnace atomic absorption spectroscopy
L	liter
MEA	monoethanol amine
mg	milligram
min	minute
mL	milliliter
n	number of analyses
PE	Perkin Elmer
pg	picogram
QC	quality control
RCRA	Resources Conservation and Recovery Act
s	second
TCLP	Toxicity Characteristics Leaching Procedure

Symbols Used in this Report

°C	degrees Centigrade
μg	microgram
μL	microliter
%	percent
σ	standard deviation of the population

Analysis of Chromium in Amine/Glycol Solutions

by P.L. Sibrell¹, S.R.M. Burton¹, and D.E. Cornelius¹

Abstract

A procedure has been developed for analyzing chromium in the amine/glycol gas-treating solution from the Exell Helium Plant in Masterson, Texas. The amine/glycol solution is used to remove carbon dioxide and water from the plant's feed stream. Chemical analysis of the solution is difficult because of its water-soluble organic compound content, alkalinity, viscosity, and solids content. The procedure involves two-stage dilution of the sample with water, followed by graphite furnace atomic absorption analysis for chromium content. The effects of solution viscosity, particulates, acid digestion, and other impurities are documented.

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Introduction

The Exell Helium Plant near Amarillo, Texas, which is part of the U.S. Bureau of Land Management's helium operations, produces 240 million cubic feet of helium annually. The Exell Plant uses cryogenic methods to produce helium that is up to 99.9999% pure. Prior to cryogenic treatment, water and carbon dioxide must be removed from incoming gas streams. This is accomplished by contacting the gas with a solution of 25% monoethanol amine (MEA), 70% diethylene glycol (DEG), and 5% water. The amine removes carbon dioxide from the gas stream, while the DEG decreases the water content of the gas (1). The gases are stripped out of the solution by heating, and the solution is recycled back to the gas contactor.

Due to corrosion of stainless steel vessels in the stripping process, the gas-treating solution at the Exell Plant became contaminated with chromium (Cr). Because Cr is toxic, Cr levels in wastes are regulated under the Resource Conservation and Recovery Act (RCRA) (2). A substance is classified as a hazardous waste if more than 5 mg/L of Cr are released in the Toxicity Characteristic Leaching Procedure (TCLP) (3). For liquids with less than 0.5% solids, the liquid itself is classed as the extract and must not contain more than 5 mg/L of Cr if the liquid is to be disposed of as a nonhazardous waste.

In order to assess Exell's amine/glycol solution and apply corrective action, the concentration of Cr had to be measured. Because of degradation and contamination, the amine/glycol solution had become very dark and viscous and also contained particulates. Thus, the sampling and preparation of the solution were critical to accurate analytical results. This paper describes the development of a procedure to analyze samples for Cr.

Experimental

The amine/glycol samples were analyzed for Cr content using graphite furnace atomic absorption spectroscopy (GFAAS) (4 and 5). A Perkin-Elmer² (PE) 5100 PC atomic absorption spectrometer with a 5100 ZL Zeeman furnace module was used to analyze all samples. The spectrometer was equipped with an automated sampler for injecting solutions into the furnace, and was controlled by PE software running on a personal computer that was interfaced with the furnace, autosampler, and spectrometer. The spectrometer was serviced by a PE engineer before sample analysis began. The furnace temperature program was the PE default (Table 1). For each analysis, 20 μL of the sample were injected into the graphite furnace, along with 5 μL of the matrix modifier. The matrix modifier, which stabilizes the thermal ingredients, contained 15 μg of magnesium nitrate, as recommended in the standard conditions for Cr analysis. Special high-purity nitric acid and magnesium nitrate were used for sample acidification and matrix modification. High-purity deionized water was used to prepare the solutions and rinse the glassware. All other reagents were analytical-grade.

² Reference to specific products does not imply endorsement by the U.S. Bureau of Land Management.

Table 1. Graphite furnace temperature program.

Step	Temp., °C	Ramp Time, s	Hold Time, s	Ar Flow, mL/min	Read
1	110	1	20	250	-
2	130	5	30	250	-
3	1500	10	20	250	-
4	2300	0	5	0	On
5	2400	1	2	250	-

For each analytical run on the spectrometer, a calibration curve was generated using blank, 20- $\mu\text{g/L}$, and 40- $\mu\text{g/L}$ Cr standards prepared from a 1,000-mg/L stock solution. The autosampler also generated 10- $\mu\text{g/L}$ and 30- $\mu\text{g/L}$ standards by diluting the 20- $\mu\text{g/L}$ and 40- $\mu\text{g/L}$ standards. The software calculated a nonlinear, zero-intercept, best-fit curve for the data. Sample concentrations were then read directly during analysis. A check sample prepared by diluting a PE mixed-metal standard was used for quality control (QC) purposes in each run.

The characteristic mass is the amount of analyte injected into the graphite furnace that results in an absorbance of 1% (5). This quantity should not vary widely from laboratory to laboratory, and is therefore a good indicator of instrument performance. The characteristic mass calculated for Cr during standardization was 8 pg, which was well within the acceptable range of $7 \text{ pg} \pm 20\%$, demonstrating good instrument performance and standard preparation.

Several test solutions were used in the development of the analytical procedure. A synthetic solution was prepared by mixing reagent-grade DEG, MEA, and water in proportions that simulated the Exell Plant solution. A similar solution was spiked with a weighed amount of potassium dichromate, resulting in 110 mg/L of Cr. Two actual samples from the circulating solution at the Exell Plant were also used. These samples were taken on 3/28/96 and 6/27/96. Replicate samples from both of these solutions were run to test the accuracy and precision of the method.

Method Development

Previous analysis by a commercial laboratory showed Cr levels of up to 10 to 20 mg/L in selected samples of Exell solution. Graphite furnace analysis is typically done in the $\mu\text{g/L}$ range, so the samples had to be diluted before analysis, which was beneficial for decreasing sample matrix effects. A two-stage dilution procedure was adopted because of the high viscosity of the samples. In the first stage, 5 mL of solution was pipetted into a 100-mL volumetric flask using a

glass pipet. The pipets were allowed to sit for approximately 10 minutes so that the viscous solution was drained. The samples were then diluted to volume with water. In the second stage, a 1-mL aliquot was taken with an Eppendorf micropipettor and diluted to 50 mL in a volumetric flask. This resulted in an overall dilution of a thousandfold. Two drops of high-purity nitric acid were added to the final dilution to stabilize the metal content, giving the solution a roughly 0.2% nitric acid matrix.

The dilution procedure was used on the test solutions described in the previous section. Table 2 shows the results in terms of the mean concentration [Cr] (mg/L), the number of analyses (n), and the standard deviation of the population (σ).

Table 2. Analysis of test solutions.

Sample	[Cr], mg/L	n	σ
Synth. soln. blank	2.7	6	0.9
Synth. soln. spike	120	4	9.
Exell, 3/28	11	13	0.4
Exell, 6/27, repl. A	17	6	0.9
Exell, 6/27, repl. B	17	9	1.4

The measurements for the blank and spike solutions were probably slightly high because these solutions were not prepared with high-purity water. However, the results are encouraging, because they show that the sample matrix did not severely affect the analysis. For the samples in general, the standard deviation indicated a high level of precision for this method. The QC checks were always within 5% of the 20- μ g/L standard.

Because of the high viscosity of the amine/glycol solutions, there was a possibility of significant error in the first stage of dilution. The error was estimated by analyzing the amount of solution left in the pipet after use. The "dirty" pipet was rinsed with water into a second 100-mL volumetric flask, diluted to volume with water, and analyzed. Two pipets used to dispense the 6/27/96 Exell sample were tested. A pipet used to dispense an aqueous standard containing 10 mg/L of Cr was also tested. Based on the Cr content of the rinse solution, the pipet used for the aqueous standard retained 45 μ L of solution. The pipets used to dispense the Exell samples retained 100 and 110 μ L of solution. The amount of solution left in the pipet due to incomplete drainage was about 50 μ L, which is 1% of the original 5-mL sample volume. Therefore, this error was determined to be negligible.

Atomic absorption analyses can be subject to errors arising from differences in sample matrices. These errors will be minimized when the sample matrices are as similar as possible.

Wherever possible, samples and standards were prepared with a background of 0.2% nitric acid. Disposable plastic eyedroppers were used that dispensed approximately 20 drops per mL. Therefore, four drops of acid were added per 100 mL of solution. High-purity acid was used to minimize contamination of the solutions. However, the alkalinity of the amine in many cases neutralized the standard acid addition. This was not noticeable at a 1,000:1 dilution, but became significant at a 100:1 dilution. For a 100:1 dilution, 15 drops of acid were required. Unusual samples were checked with pH paper and acid was added until the pH was less than 2.

Independent analysis showed that the Exell samples contained significant amounts of dissolved iron. There was some concern that the iron might interfere with the Cr analysis. Therefore, the effect of iron concentration was measured by preparing three samples containing 20 µg/L of Cr, and 100, 1,000, and 10,000 µg/L of iron, respectively. All three samples were found to contain 20 ± 1 µg/L of Cr, indicating that iron did not interfere with the analysis.

Some of the samples contained particulate matter. Separate analysis of the particulate matter was performed by an outside laboratory using x-ray diffraction. The material was found to be a mixture of the iron oxides magnetite and maghemite. Typically, samples were allowed to settle for 24 hours before pipetting an aliquot for analysis. However, it was desired to test whether the particulates would affect the results. Therefore, a set of samples was prepared for analysis from the Exell 6/27/96 sample. The sample was mixed thoroughly, either by agitation or hand shaking, and three different aliquots were taken immediately. Two more samples were taken after the solution was allowed to settle overnight. One aliquot was filtered through Whatman glass-fiber filter paper (grade GF/F) prior to dilution and analysis. The results showed no significant difference between any of these samples (Table 3), indicating that either the particulates did not contain any Cr, or that they did not release any Cr to the solution.

Table 3. Analysis of stirred solutions.

Sample	[Cr], mg/L	n	σ
Exell, 6/27, mixed, A	14	5	0.6
Exell, 6/27, mixed, B	14	2	0.0
Exell, 6/27, mixed, C	16	2	0.5
Exell, 6/27, settled, A	14	2	0.5
Exell, 6/27, settled, B	14	3	0.0
Exell, 6/27, filtered	15	2	0.0

Acid digestions are commonly used to ensure that metal complexes are broken down and available for analysis. Up to this point, no acid digestions had been performed on Exell samples under the assumption that the Cr was already in a soluble state; however, that assumption needed to be investigated. A local commercial laboratory had used an acid-digestion procedure based on the Environmental Protection Agency's method 3010A of SW-846 (6) prior to inductively coupled plasma analysis of Exell samples. This procedure involves adding 5 mL of hydrochloric acid and 3 mL of nitric acid, heating and evaporating to one-half the original volume, then rediluting to volume with water. The procedure was repeated in our laboratory with only nitric acid; hydrochloric acid is not recommended for digestions for graphite furnace analysis because of the volatility of many metal chlorides. The digested samples were then diluted and analyzed using the temperature program and modifiers described. There was no significant difference between digested and undigested samples in this first digestion (Table 4).

At this point, the possibility was raised that the amine in the samples had neutralized the relatively small amount of acid added. This was confirmed by checking the pH of the digestate, which proved to be about 10. Therefore, another set of digestions was done, this time by first diluting 5 mL of solution into about 100 mL of deionized water, then adding 5 mL of nitric acid and heating to low volume. Two aliquots of the Exell 6/27 sample were taken, one from a filtered sample and one from an unfiltered, well-stirred sample. The acid addition and heating steps were repeated twice. The color of the solutions lightened significantly as the digestion proceeded. When the digested samples were diluted and analyzed, there was still no significant difference between undigested and digested samples (Table 4), leading to the conclusion that the digestion was not necessary.

Table 4. Analysis of digested solutions.

Sample	[Cr], mg/L	n	σ
Exell 3/28, digest 1	11	8	0.0
Exell 6/27, digest 1	14	8	0.5
Exell 6/27, stirred, digest 2	17	2	0.5
Exell 6/27, filtered, digest 2	14	2	0.0

The spectrometer has the capacity to add spikes of Cr by injecting a given volume of Cr standard with the sample. This was done as a QC check on many of the day-to-day runs on the spectrometer. Over a period of about 2 months, 22 samples were analyzed in this manner. The Cr spike recoveries averaged 99%, with a standard deviation of $\pm 12\%$. These results confirmed that the spectrometer was indeed picking up all the Cr present in the samples. Therefore, the standard procedure for analysis of solution system samples was two-stage dilution into a 0.2% nitric acid matrix, followed by analysis using GFAAS.

As a final check, the effectiveness of this procedure was confirmed by adding spikes of 10 and 20 mg/L of Cr to aliquots of the 6/27 Exell sample. The samples were run as above; spike recovery was within the range of 90 to 110%, indicating good recovery of Cr and vindicating the procedure (Table 5).

Table 5. Analysis of spiked solutions.

Sample	[Cr], mg/L	n	σ
Exell 6/27 (from Table 3)	14	3	0.0
Exell 6/27 + 10 mg/L spike	24	3	0.0
Exell 6/27 + 20 mg/L spike	33	3	1.2

Exell Sample Analysis

Over the course of the development of this method, analysis of Exell samples taken on 3/28/96 and 6/27/96 showed that the Cr concentration had increased from 11 to 15 mg/L. An archive sample from 1/26/96 was found to contain 5 mg/L of Cr, indicating that the Cr contamination was increasing. This may have been due to increased corrosion rates or introduction of contaminated material back into the system. By 9/30/96, the Cr content of the solution had risen to 48 mg/L. This qualified the solution as a hazardous waste by the TCLP provisions of RCRA. Because of this, on 9/30/96, the previously mothballed solution reclaimer was put back into service. The solution reclaimer essentially operates as a vacuum distillation system for the purification of the amine/glycol solution. Analysis of the product from the reclaimer on 10/4/96 confirmed removal of the Cr, with less than 0.1 mg/L Cr appearing in the product. The solution was sampled frequently after the reclaimer was started up; Table 6 shows the Cr concentration decreasing quickly with reclaimer operation. In fact, the Cr concentration followed the expected exponential decay calculated for the system, based on the volume of the solution and the flow rate through the reclaimer, as shown in Figure 1.

By 10/30/96, the Cr level in the solution had decreased to 1 mg/L, the color had lightened, and the viscosity decreased. The hazardous Cr content had been transferred to the much smaller volume, from the 12,000 gallons of the entire solution inventory to about 2,000 gallons in the reclaimer bottoms tank. Analysis of material taken from the top of the tank showed about 230 mg/L of Cr, while a sample from the bottom of the tank showed 270 mg/L. The reclaimer bottoms will be disposed of by solidification with flyash, which will be described in a later publication.

Table 6. Analysis of Exell Plant solutions.

Sample	[Cr], mg/L
Lean, 1/26	5
Lean, 3/28	11
Lean, 6/27	14
Lean, 9/30	48
Lean, 10/9	25
Lean, 10/11	6
Lean, 10/15	2
Lean, 10/30	1
Lean, 11/6	1.0
Lean, 12/10	2.7
Reclaimer product, 10/4	< 0.1
Reclaimer tank bottom, 10/30	270
Reclaimer tank top, 12/10	230

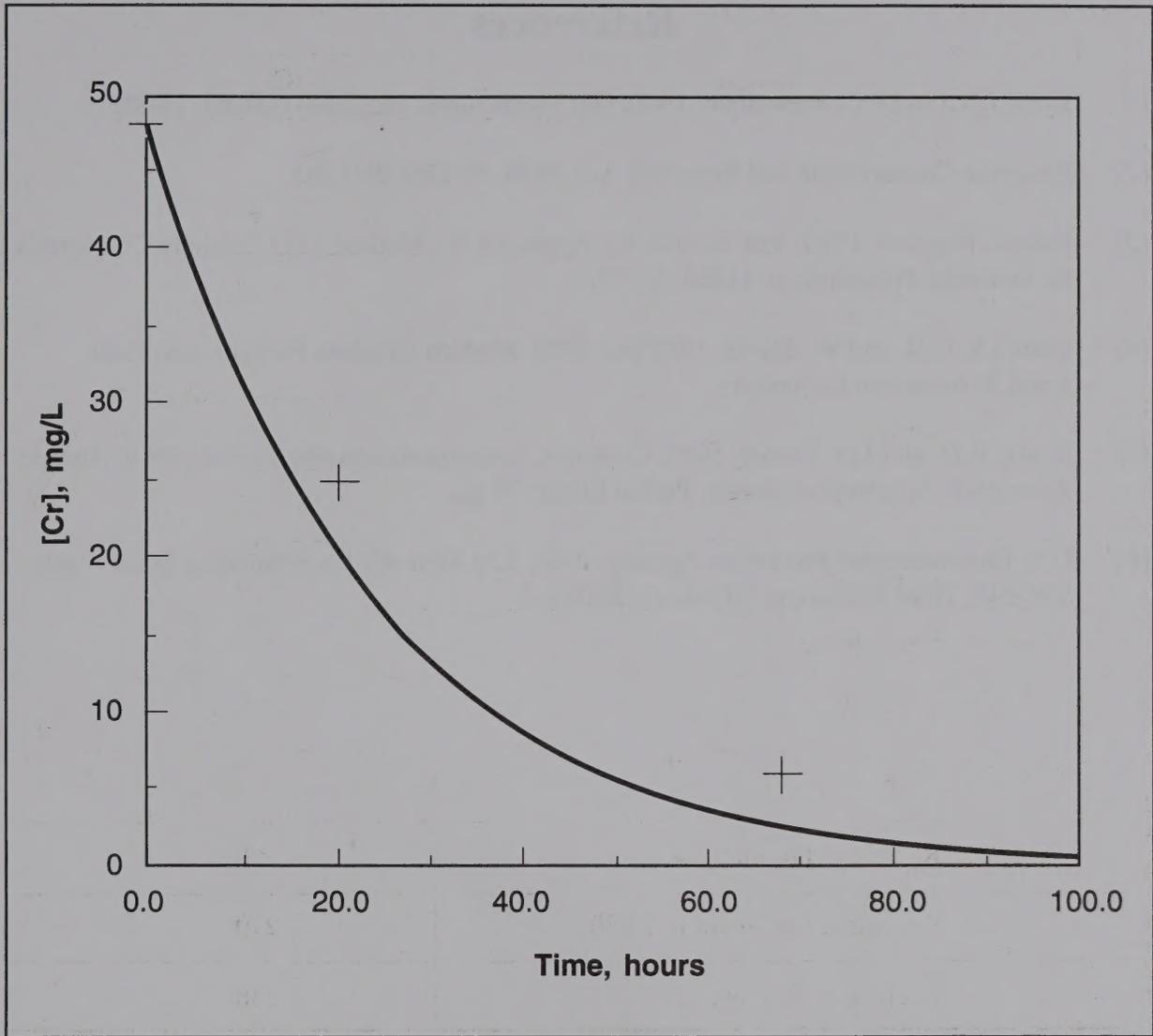


Figure 1. Chromium concentration in amine/glycol solution as a function of reclaimer hours of operation. Solid line = calculated result; “+” = analytical result.

References

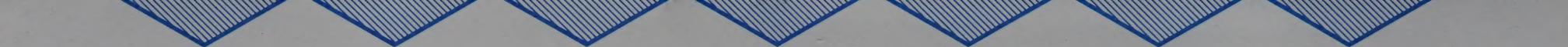
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